#### TITLE OF THE INVENTION

# CHARGING DEVICE, AND PROCESS CARTRIDGE AND IMAGE FORMING APPARATUS USING THE CHARGING DEVICE

#### BACKGROUND OF THE INVENTION

# Field of the Invention

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The present invention relates to a charging device which charges an image bearing member with a charging roller in electrophotographic image forming apparatus and which has a cleaner cleaning the charging roller. In addition, the present invention also relates to an image forming apparatus such as copiers and printers which use the cleaning device and a process cartridge using the charging device.

# 15 Discussion of the Background

In conventional electrophotographic image forming apparatus, an image is typically formed by the following method:

- (1) an image bearing member such as photoreceptors is charged with a charger to apply a charge having a predetermined polarity to the image bearing member (i.e., charging process);
- (2) the image bearing member is exposed to imagewise light to form an electrostatic latent image on the image bearing member (i.e., light irradiation process);
- 25 (3) the electrostatic latent image is developed with a toner having a charge with the same polarity as that of the electrostatic latent image to form a toner image (i.e.,

developing process);

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- (4) the toner image is transferred to a receiving material such as papers (i.e., transferring process); and
- (5) the toner image is fixed on the receiving material upon application of heat and pressure thereto to form a hard copy (i.e., fixing process).

Even after the transfer process, a small amount of toner particles remain on the surface of the image bearing member. Therefore, the surface of the image bearing member is typically cleaned by a cleaner such as cleaning blades and cleaning brushes before the next charging process to remove the residual toner particles from the image bearing member.

Recently, contact charging methods in which a voltage is applied to an image bearing member by an electroconductive charging roller which is contacted with the image bearing member or short-range charging methods in which a voltage is applied to an image bearing member by an electroconductive charging roller which is set in close vicinity to an image bearing member are typically used for the charging process. This is because these charging methods have advantages such that the amount of ozone generated due to discharging caused by the charger, and the power consumption of the charger can be reduced.

However, when residual toner particles are insufficiently removed, a problem in that the remaining toner particles adhere to the contact charging roller or the short-range charging roller occurs. This is because the remaining toner particles typically include toner particles

having a charge with a polarity opposite to the polarity of the potential of the charging roller, and the reversely-charged toner particles are attracted by the charging roller, resulting in adhesion of the toner particles on the surface of the charging roller. In addition, dust such as paper dust generated by receiving papers, which has a charge with a polarity opposite to that of the potential of the charging roller is also adhered to the charging roller.

Recently a need exists for an electrophotographic image forming apparatus capable of producing high quality and high definition images. Therefore, a spherical toner having a relatively small particle diameter is typically used to form a toner image in which such small spherical toner particles can be densely adhered to an electrostatic latent image. However, such a small spherical toner has a drawback in that when toner particles remaining on an image bearing member are scraped by a cleaning blade, the toner particles often pass through the nip between the image bearing member and the cleaning blade, resulting in occurrence of bad cleaning of the surface of the image bearing member (namely, the charging roller is contaminated with toner particles). Therefore, it is necessary to clean the surface of the charging roller to prevent occurrence of various problems.

Published unexamined Japanese Patent Application No. 2002-221883 discloses a cleaning device for a charging roller in which a brush roller is brought into contact with a charging roller upon application of only its own weight thereto while

being driven by the rotating charging roller. The length of the fibers serving as the hair of the brush roller is not longer than 2 mm, and preferably from 0.4 to 0.6 mm. Such a brush roller can be prepared by a method in which short fibers are planted on a roller by utilizing electrostatic force.

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However, when the length of the fibers on the brush roller is short, the amount of toner particles that the brush roller can contain in the hair is limited. In a case of process cartridges including a charging roller, the charging roller has to have the same life as those of other members constituting the process cartridges, each of which has a relatively long life. Therefore, a cleaning device having such a brush roller is not suitable for such process cartridges.

In addition, it is necessary for the cleaning device to remove foreign materials such as paper dust, which adhere to the charging roller.

Because of these reasons, a need exists for a charging device with a cleaner which can efficiently clean materials electrostatically adhered to the surface of a charging roller over a long period of time.

## SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a charging device with a cleaner which can efficiently clean materials electrostatically adhered to the surface of a charging roller over a long period of time.

Another object of the present invention is to provide a process cartridge and an image forming apparatus, which can produce high quality and high definition images over a long period of time.

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Briefly these objects and other objects of the present invention as hereinafter will become more readily apparent can be attained by a charging device including a charging roller having a metal cylinder and an elastic layer located on the metal cylinder, a cleaner configured to clean the charging roller, and a member configured to impart substantially the same potential as that of the charging roller to an electroconductive brush roller of the cleaner when s bias is applied to the charging roller. The cleaner includes the electroconductive brush roller having a roller and hair located overlying of a roller of the electroconductive brush roller. The hair include a fiber which has a width of from 0.1 to 20 denier, and a length of from 0.3 to 2.5 mm and which is planted at a density of from 7,000 to 46,000 lines/cm<sup>2</sup>.

The electroconductive brush roller preferably has an  $^{\cdot}$  20 electric resistance of from 10 to 10  $^{8}$   $\Omega_{\cdot}$ 

The fiber is preferably a nylon fiber.

The hair is preferably subjected to a back coat treatment in which a bunch of fiber is fixed with a foundation cloth and a roller using an electroconductive resin to impart good electroconductivity to the fiber and to fix the fiber to the roller of the brush roller.

It is preferable that the member is a blade spring

configured to connect the shaft of the brush roller with the shaft of the charging roller.

The electroconductive brush roller preferably rotates together with the charging roller while being driven by the charging roller. Alternatively, the brush roller can rotate so as to counter the charging roller at their contact point.

The cleaner preferably has an oscillating device configured to oscillate the brush roller in the longitudinal direction thereof.

The cleaner can have a one-way clutch on the shaft thereof to slightly change the contact point of the brush roller with the charging roller.

As another aspect of the present invention, a process cartridge is provided which can be detachably attached to an image forming apparatus and which includes:

at least an image bearing member configured to bear an electrostatic latent image; and

a charger configured to charge the image bearing member, wherein the charger is the charging device mentioned 20 above.

As yet another aspect of the present invention, an image forming apparatus is provided which includes:

an image bearing member;

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a charger configured to charge the image bearing member;

a light irradiator configured to irradiate the charged image bearing member with imagewise light to form an electrostatic latent image on the image bearing member;

a developing device configured to develop the electrostatic latent image with a developer including a toner to form a toner image on the image bearing member;

a transferring device configured to transfer the toner image onto a receiving material; and

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a fixing device configured to fix the toner image on the receiving material,

wherein the charger is the charging device mentioned above.

The toner preferably has a volume average particle diameter (Dv) of from 3 to 8  $\mu$ m, and a ratio (Dv/Dn) of the volume average particle diameter (Dv) to a number average particle diameter (Dn) of from 1.00 to 1.40.

In addition, each of the form factors SF-1 and SF-2 of the toner is preferably greater than 100 and not greater than 180.

The toner is preferably prepared by a method including:
dispersing or dissolving toner constituents including at
least a polyester prepolymer having a functional group having
a nitrogen atom, another polyester resin, a colorant, and a
release agent in an organic solvent to prepare a toner
constituent liquid; and

medium including a compound capable of reacting the functional group of the polyester prepolymer to crosslink and/or elongate the polyester prepolymer and to form toner particles in the aqueous medium.

It is preferable that the toner has a spherical form and satisfies the following relationships:

- $0.5 \le r2/r1 \le 1.0$ ; and
- $0.7 \le r3/r2 \le 1.0$ ,

5 wherein r1 represents a major-axis particle diameter of the toner, r2 represents a minor-axis particle diameter of the toner and r3 represents a thickness of the toner, wherein r3 ≤ r2 ≤ r1. In this case, 100 particles of the toner are observed to determine the ratios r2/r1 and r3/r2.

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These and other objects, features and advantages of the present invention will become apparent upon consideration of the following description of the preferred embodiments of the present invention taken in conjunction with the accompanying drawings.

### BRIEF DESCRIPTION OF THE DRAWINGS

Various other objects, features and attendant advantages of the present invention will be more fully appreciated as the same becomes better understood from the detailed description when considered in connection with the accompanying drawings in which like reference characters designate like corresponding parts throughout and wherein:

- Fig. 1 is a schematic view illustrating the cross section of an image forming apparatus having an embodiment of the charging device of the present invention;
  - Fig. 2 is an enlarged view of the main portion of the image

forming apparatus illustrated in Fig. 1;

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Fig. 3 is a schematic view illustrating an embodiment of the cleaner of the charging device of the present invention;

Fig. 4 is a schematic view illustrating an embodiment of the member for use in the charging device, which member imparts the same potential as that of the charging roller to the electroconductive brush roller;

Fig. 5 is an enlarged view illustrating the hairs planted on a roller of the brush roller for use in the cleaning device of the present invention;

Figs. 6A and 6B are projected images of toner particles for explaining the form factors SF-1 and SF-2 thereof; and

Figs. 7A to 7C are schematic views of a toner particle for explaining the major axis particle diameter, minor axis particle diameter and thickness of the toner particle.

### DETAILED DESCRIPTION OF THE INVENTION

The present invention will be explained referring to drawings.

Fig. 1 is a schematic view illustrating the cross section of an image forming apparatus having an embodiment of the charging device of the present invention. Fig. 2 is an enlarged view of the main portion of the image forming apparatus illustrated in Fig. 1.

An image forming apparatus (i.e., an electrophotographic copier) 100 includes a scanner unit 20 which reads the image of an original, an image forming unit 30 which reproduces the

read image on a receiving material 5, and a paper feeding unit 40 which timely feeds the receiving material 5 to the image forming unit 30. The image forming unit 30 includes a photoreceptor 1 serving as an image bearing member, and a charger 2, a light irradiator 3, a developing device 4, a transferring device 6, a fixing device 7 and a cleaning device 8, which are arranged in the vicinity of the photoreceptor 1 even after the transfer process. Numeral 9 denotes a discharger configured to irradiate the photoreceptor 1 with light to discharge charges remaining on the photoreceptor 1.

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The photoreceptor 1 includes a photoconductive material such as amorphous metals, e.g., amorphous silicon and amorphous selenium; and organic compounds such as bisazo pigments and phthalocyanine pigments. In view of environmental protection and post-treatment of the photoreceptor, the organic compounds are preferably used.

The charger 2 has a charging roller 2a having a metal cylinder and an elastic layer formed on the peripheral surface of the metal cylinder, a cleaner 2b and a power source (not shown) connected with the charging roller 2a. The power source applied a high voltage to the charging roller 2a to form a predetermined high electric field at the charging portion in which the charging roller 2a faces the photoreceptor 1. As a result, corona discharging occurs at the charging portion, and thereby the surface of the photoreceptor 1 is uniformly charged.

The cleaner has an electroconductive brush roller configured to clean the surface of the charging roller 2a. The

cleaner 2b will be explained below in detail.

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The light irradiator 3 converts the data, which are read by a scanner in the scanner unit 20 or which are sent from an external device such as personal computers, to image data. The light irradiator 3 irradiates the surface of the photoreceptor 1 with imagewise laser light 3a via an optical system (not shown) including a polygon mirror, mirrors, lens and the like.

The developing device 4 has a developer bearing member 4a which bears a developer including a toner to supply the developer to the photoreceptor 1, a toner supplying room, a developer regulator configured to control the thickness of the developer layer formed on the developer bearing member 4a and other members. The developer bearing member 4a is arranged in close vicinity to the photoreceptor 1 while a small gap is formed therebetween.

The developer bearing member 4a includes a cylindrical developer bearing member which is rotatably supported and a magnetic roller which is fixed inside the cylindrical developer bearing member so as to be coaxial to the cylindrical developer bearing member. The developer bearing member 4a transports the developer while bearing the developer on the peripheral surface using a magnetic force of the magnetic roller. The developer bearing member 4a is electroconductive and is made of a nonmagnetic material. In addition, a power source is connected with the developer bearing member 4a to apply a developing bias thereto. Namely, a voltage is applied to the developer bearing member 4a to form an electric field between the photoreceptor

1 and the developer bearing member 4a.

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The transfer device 6 includes a transfer belt 6a, a transfer bias roller 6b, and a tension roller 6c. The transfer bias roller 6b has a metal cylinder and an elastic layer formed on the metal cylinder. When a toner image is transferred from the photoreceptor 1 to the receiving material 5, a pressure is applied to the transfer bias roller 6b to press the receiving material 5 to the photoreceptor 1.

The transfer belt 6a is a seamless belt made of a material having a high heat resistance, such as polyimide films. A fluorine-containing resin layer can be formed on the outermost surface of the transfer belt 6a. In addition, a silicone rubber layer can also be formed between the base material of the transfer belt and the fluorine-containing resin layer. The tension roller 6c is provided to rotate the transfer belt 6b while tightly stretching the transfer belt 6b.

The fixing device 7 includes a fixing roller having a heater such as halogen lamps therein and a pressure roller which is pressure-contacted with the fixing roller. The fixing roller has a metal cylinder, an elastic layer (e.g., silicone rubber layers) having a thickness of from 100 to 500  $\mu m$  (preferably about 400  $\mu m$ ), and a outermost resin layer including a releasing resin such as fluorine-containing resins. The outermost resin layer is typically formed using a resin tube such as tetrafluoroethylene / perfluoroalkylvinyl ether copolymer (PFA) tubes. The thickness of the outermost resin layer is preferably from 10 to 50  $\mu m$ . A temperature detector

is provided on the peripheral surface of the fixing roller to measure the temperature of the surface of the fixing roller and to control the temperature so as to be in a range of from about 160~°C to about 200~°C.

The pressure roller includes a metal cylinder and an offset preventing layer formed on the metal cylinder. The offset preventing layer is typically made of a material such as tetrafluoroethylene / perfluoroalkylvinyl ether copolymers (PFA) and polytetrafluoroethylene (PTFE). Similarly to the fixing roller, an elastic layer can be formed between the metal cylinder and the offset preventing layer.

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The cleaning device 8 for cleaning the photoreceptor 1 includes a first cleaning blade 8a and a second cleaning blade 8b which is located on the downstream side from the first cleaning blade 8a relative to the rotating direction of the photoreceptor 1. In addition, the cleaning device 8 also includes a collection member 8d configured to collect the toner particles obtained by cleaning, a collection coil 8c configured to transport the collected toner particles, and a container (not shown) configured to contain the collected toner particles.

The first cleaning blade 8a is made of a material such as metals, resins and rubbers. Among these materials, rubbers such as fluorine-containing rubbers, silicone rubbers, butyl rubbers, butadiene rubbers, isoprene rubbers and urethane rubbers are preferably used. In particular, urethane rubbers are more preferably used. The first cleaning blade 8a mainly removes toner particles remaining on the surface of the

photoreceptor 1 after the transferring process.

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The second cleaning blade 8b mainly removes materials such as additives included in the toner, which adhere to the surface of the photoreceptor 1 like a film. The second cleaning blade 8b can be made of the same material as that of the first cleaning blade 8a but typically includes an abrasive to effectively remove the film materials formed on the photoreceptor 1.

Then the cleaner of the charging device of the present invention which cleans the surface of the charging roller will be explained.

Fig. 3 is a schematic view illustrating the charging device of the present invention having a cleaner. The cleaner 2b includes an electroconductive brush roller 20 which is arranged on the upper portion of the charging roller 2a. Both ends of a shaft of the electroconductive brush roller 20 are slidably engaged with respective guide slots 12 formed on respective bearing members 11. Therefore, the brush roller 20 is brought into contact with the charging roller 2a upon application of its own weight to the brush roller 20. In addition, since the ends of the shaft of the brush roller 20 are rotatably engaged with the guide slots 12, the brush roller 20 is rotated in a direction indicated by an arrow while driven by the charging roller 2a.

Since the brush roller 20 is driven by the charging roller 2a, it is not necessary to provide a driving device of the brush roller 20, and thereby the configuration of the cleaner 2b can

be simplified. In addition, it is avoided to press the charging roller 2a with the brush roller 20 at an excessive pressure, and thereby abrasion of the surface of the charging roller 2a can be prevented.

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The brush roller 20 has hair thereon, in which fiber having a thickness of from 0.1 to 20 denier and a length of from 0.3 to 2.5 mm are planted at a density of from 7,000 to 46,000 fibers/cm<sup>2</sup>. When the fiber is too thin, the hair tends to be fell down when the brush roller 20 is brought into contact with the charging roller 2a. In contrast, when the fiber is too thick, the density of the fiber decreases, resulting in deterioration of cleaning efficiency of the cleaner.

When the density of the fibers is too low, the cleaning efficiency deteriorates. In contrast, when the density is too high, the spaces in the hair for containing collected toner particles decrease. When the fiber is too long, the hair is fell down when the brush roller 20 is brought into contact with the charging roller 2a.

By using the brush roller 20 having such hair as mentioned above, the surface of the charging roller 2a can be efficiently cleaned while a large amount of collected toner particles can be contained in the hair.

The cleaner 2 has a member which imparts substantially the same potential as that of the charging roller 2a to the brush roller 20 when a charging bias voltage is applied to the charging roller 2a to charge the photoreceptor 1. In general, the materials adhered to the charging roller 2a have a charge with

a polarity opposite to that of the charging bias voltage. Specifically the materials are, for example, reversely-charged toner particles remaining on the photoreceptor 1 and dust such as paper dust which are electrostatically attracted by the charging roller 2a. By providing the member mentioned above on the brush roller 20, the materials adhered to the charging roller 2a can be easily and effectively transferred to the brush roller 20 by the mechanical removing action and the electrostatic removing action of the brush roller 20.

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Specific examples of the mechanism include devices which applied a bias to the brush roller. However, in view of space saving, a member illustrated in Fig. 4 is preferably used for the cleaner.

Fig. 4 is an embodiment of the member which can impart the same potential as that of the charging roller 2a to the brush roller 20. Referring to Fig. 4, the shaft of the brush roller 20 is connected with the shaft of the charging roller 2a using blade springs 13. The bias applied to the shaft of the charging roller 2a is also applied to the shaft of the brush roller 20 via the blade springs 13, and thereby the brush roller 20 has substantially the same potential as that of the charging roller 2a.

In order that the brush roller 20 has the same potential as that of the charging roller 2a, the electric resistance of the brush roller 20 is preferably from 10 to  $10^8~\Omega$ .

Specific examples of the material for use in the hair of the brush roller 20 include nylon resins, triacetate resins, acrylic resins and TEFLON®. Among these materials, nylon resins are preferably used in view of cost and cleanability.

Fig. 5 is an enlarged view illustrating the hair of the brush roller 20. A bunch of fiber 14 is connected with a foundation cloth 15 by double stitching as illustrated in Fig. 5. The fiber is preferably subjected to a back coat treatment in which a bunch of fiber 14 is fixed with a foundation cloth 15 using an electroconductive resin to impart good electroconductivity to the fiber 14 and to fix the fiber 14 to the roller of the brush roller 20. The foundation cloth 15 with the fiber 14 is adhered to a roller (or a shaft) with an electroconductive adhesive 16 to prepare the brush roller 20. By subjecting the fiber to such a back coat treatment, the hair can be fixed to the roller, and thereby the life of the brush roller 20 can be prolonged.

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In Fig. 3, the brush roller 20 is rotated while driven by the charging roller 2a, i.e., the brush roller 20 rotates in a direction (i.e., counterclockwise) opposite to that (clockwise direction) of the charging roller 2a. However, the brush roller 20 can be rotated so as to counter the charging roller 2a at their contacting portion, i.e., the brush roller 20 can be rotated in the same direction as that of the charging roller 2a. By rotating the brush roller 20 in the same direction as that of the charging roller 2a, the mechanical cleaning ability of the brush roller 20 can be further improved.

In order to rotate the brush roller 20 in the same direction as that of the charging roller 2a, a mechanism in which

the rotation of the charging roller 2a is transferred to a gear provided on the shaft of the brush roller 20 with a gear therebetween is typically used.

In addition, the cleaner 2b preferably has an oscillating mechanism configured to oscillate the brush roller 20 in the longitudinal direction of the brush roller 20. For example, a bearing is provided on the tip of the shaft of the brush roller 20 so as to face the surface of an oscillating cam of a gear. When the charging roller 2a rotates, the gear with the oscillating cam is also rotated, and thereby the brush roller 20 is oscillated in the longitudinal direction of the brush roller 20.

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By oscillating the brush roller 20, the surface of the charging roller 2a can be uniformly cleaned. In particular, paper dust is typically generated from both edge portions of receiving papers, and therefore paper dust is mainly adhered to edge portions of the photoreceptor 1. The paper dust is then transferred to the edge portions of the charging roller 2a. By oscillating the brush roller 20, such paper dust can be easily removed from the charging roller 2a.

Alternatively, a one-way clutch can be provided on the shaft of the brush roller 20. During the image forming operations are performed, the one-way clutch is locked, i.e., the brush roller is stopped. Therefore, the charging roller 2a is cleaned while rubbed by the stopped brush roller 20. After the image forming operations, the photoreceptor 1 is stopped while slightly rotated reversely. At this point, the brush

roller 20 is also slightly rotated via the one-way clutch and then stopped. By using such a mechanism, it is prevented that the brush roller 20 is contacted with the charging roller at an excessive pressure, and thereby abrasion of the surface of the charging roller 2a can be prevented. In addition, the contact surface of the brush roller 20 with the charging roller 2a can be changed little by little, and thereby cleaning can be well performed at any time.

The above-mentioned cleaner for cleaning a charging roller can be used for not only the image forming apparatus but also a process cartridge which includes at least a photoreceptor and a charger, optionally together with one or more devices such as developing devices and photoreceptor-cleaning devices. Specifically, the above-mentioned cleaner for cleaning a charging roller is also provided on the charger of the process cartridge. By providing the cleaner, the surface of the charging roller can be cleaned and charging is well performed over a long period of time. Thus, the life of the charging roller can be prolonged so as to be the same as that of the other devices and members of the process cartridge.

The image forming apparatus of the present invention having the charging device with the cleaner is not limited to the embodiment mentioned above. For example, an image forming apparatus including an intermediate transfer medium which bears a toner image transferred from a photoreceptor to retransfer the toner image to a receiving material; an image forming apparatus including a plurality of photoreceptors to produce

multi-color images; and the like apparatus can also be included in the scope of the present invention.

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The toner for use in the image forming apparatus of the present invention preferably has a volume average particle diameter (Dv) of from 3 to 8  $\mu m$ , and a ratio (Dv/Dn) of the volume average particle diameter (Dv) to the number average particle diameter (Dn) is preferably from 1.00 to 1.40. Namely, a toner having a relatively small particle diameter and a narrow particle diameter distribution is preferably used. By using a toner having a small particle diameter, the toner can be densely adhered to an electrostatic latent image without being protruded from the latent image, and thereby high density and high quality image can be produced. By using a toner having a narrow particle diameter distribution, the charge quantity of the toner particles can be uniformed, and thereby high quality images without background development can be produced. In addition, the transferability of the toner can also be improved, and thereby the quantity of the toner particles remaining on the photoreceptor can be reduced, resulting in extension of the life of the cleaner for cleaning the charging roller.

The toner for use in the image forming apparatus preferably has a spherical form such that the form factors SF-1 and SF-2 of the toner fall in the specific ranges mentioned below. Figs. 6 are schematic views for explaining the form factors SF-1 and SF-2.

As illustrated in Fig. 6A, the form factor SF-1 represents

the degree of the roundness of a toner and is defined by the following equation (1):

$$SF-1 = \{ (MXLNG)^2 / (AREA) \} \times (100 \pi / 4)$$
 (1)

wherein MXLNG represents a diameter of the circle

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circumscribing the image of a toner particle, which image is obtained by observing the toner particle with a microscope; and AREA represents the area of the image.

When the SF-1 is 100, the toner particle has a true spherical form. It can be said that as the SF-1 increases, the toner form differs much from the true spherical form.

As illustrated in Fig. 6B, the form factor SF-2 represents the degree of the concavity and convexity of a toner particle, and is defined by the following equation (2):

$$SF-2 = \{ (PERI)^2 / (AREA) \} \times (100/4\pi)$$
 (2)

wherein PERI represents the peripheral length of the image of a toner particle observed by a microscope; and AREA represents the area of the image.

When the SF-2 is 100, the surface of the toner particle does not have concavity and convexity. It can be said that as the SF-2 increases, the toner surface is much roughened.

The form factors SF-1 and SF-2 are determined by the following method:

- (1) a photograph of particles of a toner is taken using a scanning electron microscope (S-800, manufactured by Hitachi Ltd.); and
- (2) particle images of 100 toner particles are analyzed using an image analyzer (LUZEX 3 manufactured by Nireco Corp.).

The toner for use in the image forming apparatus preferably has a form factor SF-1 greater than 100 and not greater than 180 and a form factor SF-2 greater than 100 and not greater than 180. When the toner has a particle form near the true spherical form, the contact area of a particle of the toner with another particle of the toner decreases, resulting in decrease of the adhesion between the toner particles, and thereby the toner has good fluidity. In addition, the contact area of a particle of the toner with the photoreceptor also decreases, resulting in decreases of the adhesion of the toner particle to the photoreceptor, and thereby the transferability of the toner improves. On the other hand, a spherical toner having form factors SF-1 and SF-2 of 100 tends to invade into the gap between the first cleaning blade 8a and the photoreceptor 1, and thereby the toner preferably has form factors SF-1 and SF-2 greater than 100. When the form factors SF-1 and SF-2 are too large, a toner scattering problem in that toner particles are scattered around toner images tends to occur, resulting in deterioration of the image qualities. Therefore, it is preferable that the form factors SF-1 and SF-2 do not exceed 180.

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The toner for use in the image forming apparatus of the present invention is preferably prepared by the following method:

25 (1) toner constituents including at least a polyester prepolymer having a functional group having a nitrogen atom, another polyester resin, a colorant and a release agent are dissolved or dispersed in an organic solvent to prepare a toner constituent liquid; and

(2) the toner constituent liquid is dispersed in an aqueous medium including a compound which can be reacted with the polyester prepolymer to crosslink and/or elongate the polyester prepolymer and to prepare toner particles.

Then the toner constituents and toner manufacturing method will be explained in detail.

### Modified polyester resin

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The toner of the present invention includes a modified polyester resin (i) as a binder resin. The modified polyester resin (i) is preferably prepared by crosslinking and/or elongating a polyester prepolymer having a functional group having a nitrogen atom with a compound such as amines.

The modified polyester resin (i) means a polyester resin having a group other than the ester group; or a polyester resin in which a resin component other than the polyester resin is bonded with the polyester resin through a covalent bonding or an ionic bonding. Specifically the modified polyester resin means polyester resins which are prepared by incorporating a functional group such as an isocyanate group, which can be reacted with a carboxyl group or a hydroxyl group, in the end portion of a polyester resin and reacting the polyester resin with a compound having an active hydrogen atom.

Suitable modified polyester resins for use as the modified polyester resin (i) include reaction products of a polyester prepolymer (A) having an isocyanate group with an

amine (B) can be used. As the polyester prepolymer (A) having an isocyanate group, for example, polyesters prepared by a method in which a polycondensation product of a polyol (PO) and a polycarboxylic acid (PC) which has a group having an active hydrogen is reacted with a polyisocyanate (PIC) can be used.

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Suitable groups having an active hydrogen include a hydroxyl group (an alcoholic hydroxyl group and a phenolic hydroxyl group), an amino group, a carboxyl group, a mercapto group, etc. Among these groups, alcoholic hydroxyl groups are preferable.

Suitable polyols (PO) include diols (DIO) and polyols (TO) having three or more hydroxyl groups. It is preferable to use diols (DIO) alone or mixtures in which a small amount of a polyol (TO) is added to a diol (DIO).

Specific examples of the diols (DIO) include alkylene glycol (e.g., ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol and 1,6-hexanediol); alkylene ether glycols (e.g., diethylene glycol, triethylene glycol, dipropylene glycol, polyethylene glycol,

polypropylene glycol and polytetramethylene ether glycol); alicyclic diols (e.g., 1,4-cyclohexane dimethanol and hydrogenated bisphenol A); bisphenols (e.g., bisphenol A, bisphenol F and bisphenol S); adducts of the alicyclic diols mentioned above with an alkylene oxide (e.g., ethylene oxide, propylene oxide and butylene oxide); adducts of the bisphenols mentioned above with an alkylene oxide (e.g., ethylene oxide, propylene oxide and butylene oxide); etc.

Among these compounds, alkylene glycols having from 2 to 12 carbon atoms and adducts of bisphenols with an alkylene oxide are preferable. More preferably, adducts of bisphenols with an alkylene oxide, or mixtures of an adduct of bisphenols with an alkylene oxide and an alkylene glycol having from 2 to 12 carbon atoms are used.

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Specific examples of the polyols (TO) include aliphatic alcohols having three or more hydroxyl groups (e.g., glycerin, trimethylol ethane, trimethylol propane, pentaerythritol and sorbitol); polyphenols having three or more hydroxyl groups (trisphenol PA, phenol novolak and cresol novolak); adducts of the polyphenols mentioned above with an alkylene oxide; etc.

Suitable polycarboxylic acids (PC) include dicarboxylic acids (DIC) and polycarboxylic acids (TC) having three or more carboxyl groups. It is preferable to use dicarboxylic acids (DIC) alone or mixtures in which a small amount of a polycarboxylic acid (TC) is added to a dicarboxylic acid (DIC).

Specific examples of the dicarboxylic acids (DIC) include alkylene dicarboxylic acids (e.g., succinic acid, adipic acid and sebacic acid); alkenylene dicarboxylic acids (e.g., maleic acid and fumaric acid); aromatic dicarboxylic acids (e.g., phthalic acid, isophthalic acid, terephthalic acid and naphthalene dicarboxylic acids; etc. Among these compounds, alkenylene dicarboxylic acids having from 4 to 20 carbon atoms and aromatic dicarboxylic acids having from 8 to 20 carbon atoms are preferably used.

Specific examples of the polycarboxylic acids (TC) having

three or more hydroxyl groups include aromatic polycarboxylic acids having from 9 to 20 carbon atoms (e.g., trimellitic acid and pyromellitic acid).

As the polycarboxylic acid (PC), anhydrides or lower alkyl esters (e.g., methyl esters, ethyl esters or isopropyl esters) of the polycarboxylic acids mentioned above can be used for the reaction with a polyol (PO).

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Suitable mixing ratio (i.e., an equivalence ratio [OH]/[COOH]) of a polyol (PO) to a polycarboxylic acid (PC) is from 2/1 to 1/1, preferably from 1.5/1 to 1/1 and more preferably from 1.3/1 to 1.02/1.

Specific examples of the polyisocyanates (PIC) include

aliphatic polyisocyanates (e.g., tetramethylene diisocyanate, hexamethylene diisocyanate and 2,6-diisocyanate

15 methylcaproate); alicyclic polyisocyanates (e.g., isophorone diisocyanate and cyclohexylmethane diisocyanate); aromatic didicosycantes (e.g., tolylene diisocyanate and diphenylmethane diisocyanate); aromatic aliphatic diisocyanates (e.g., α, α, α', α'-tetramethyl xylylene diisocyanates); isocyanurates; blocked polyisocyanates in which the polyisocyanates mentioned above are blocked with phenol derivatives, oximes or caprolactams; etc. These

Suitable mixing ratio (i.e., [NCO]/[OH]) of a

25 polyisocyanate (PIC) to a polyester having a hydroxyl group is
from 5/1 to 1/1, preferably from 4/1 to 1.2/1 and more preferably
from 2.5/1 to 1.5/1. When the [NCO]/[OH] ratio is too large,

compounds can be used alone or in combination.

the low temperature fixability of the toner deteriorates. In contrast, when the ratio is too small, the content of the urea group in the modified polyesters decreases and thereby the hot-offset resistance of the toner deteriorates.

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The content of the constitutional component of a polyisocyanate (PIC) in the polyester prepolymer (A) having a polyisocyanate group at its end portion is from 0.5 to 40 % by weight, preferably from 1 to 30 % by weight and more preferably from 2 to 20 % by weight. When the content is too low, the hot offset resistance of the toner deteriorates and in addition the heat resistance and low temperature fixability of the toner also deteriorate. In contrast, when the content is too high, the low temperature fixability of the toner deteriorates.

The number of the isocyanate groups included in a molecule of the polyester prepolymer (A) is at least 1, preferably from 1.5 to 3 on average, and more preferably from 1.8 to 2.5 on average. When the number of the isocyanate group is too small (less than 1 per 1 molecule), the molecular weight of the resultant urea-modified polyester decreases and thereby the hot offset resistance deteriorates.

Specific examples of the amines (B), which are to be reacted with a polyester prepolymer, include diamines (B1), polyamines (B2) having three or more amino groups, amino alcohols (B3), amino mercaptans (B4), amino acids (B5) and blocked amines (B6) in which the amines (B1-B5) mentioned above are blocked.

Specific examples of the diamines (B1) include aromatic

diamines (e.g., phenylene diamine, diethyltoluene diamine and 4,4'-diaminodiphenyl methane); alicyclic diamines (e.g., 4,4'-diamino-3,3'-dimethyldicyclohexyl methane, diaminocyclohexane and isophoron diamine); aliphatic diamines (e.g., ethylene diamine, tetramethylene diamine and hexamethylene diamine); etc.

Specific examples of the polyamines (B2) having three or more amino groups include diethylene triamine, triethylene tetramine. Specific examples of the amino alcohols (B3) include ethanol amine and hydroxyethyl aniline. Specific examples of the amino mercaptan (B4) include aminoethyl mercaptan and aminopropyl mercaptan. Specific examples of the amino acids (B5) include amino propionic acid and amino caproic acid. Specific examples of the blocked amines (B6) include ketimine compounds which are prepared by reacting one of the amines B1-B5 mentioned above with a ketone such as acetone, methyl ethyl ketone and methyl isobutyl ketone; oxazoline compounds, etc. Among these compounds, diamines (B1) and mixtures in which a diamine (B1) is mixed with a small amount of a polyamine (B2) are preferable.

The mixing ratio (i.e., a ratio [NCO]/[NHx]) of the content of the prepolymer (A) having an isocyanate group to the amine (B) is from 1/2 to 2/1, preferably from 1.5/1 to 1/1.5 and more preferably from 1.2/1 to 1/1.2. When the mixing ratio is too low or too high, the molecular weight of the resultant urea-modified polyester decreases, resulting in deterioration of the hot offset resistance of the resultant toner.

The modified polyesters may include an urethane bonding as well as a urea bonding. The molar ratio (urea/urethane) of the urea bonding to the urethane bonding is from 100/0 to 10/90, preferably from 80/20 to 20/80 and more preferably from 60/40 to 30/70. When the content of the urea bonding is too low, the hot offset resistance of the resultant toner deteriorates.

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The modified polyesters (i) can be prepared, for example, by a method such as one-shot methods or prepolymer methods. weight average molecular weight of the modified polyesters (i) is not less than 10,000, preferably from 20,000 to 10,000,000 and more preferably from 30,000 to 1,000,000. When the weight average molecular weight is too low, the hot offset resistance of the resultant toner deteriorates. The number average molecular weight of the modified polyesters is not particularly limited (i.e., the weight average molecular weight should be primarily controlled so as to be in the range mentioned above) when a polyester resin (ii) which is not modified is used in combination. Namely, controlling of the weight average molecular weight of the modified polyester resins has priority over controlling of the number average molecular weight thereof. However, when a modified polyester is used alone, the number average molecular weight is from 2,000 to 15,000, preferably from 2,000 to 10,000 and more preferably from 2,000 to 8,000. When the number average molecular weight is too high, the low temperature fixability of the resultant toner deteriorates, and in addition the gloss of full color images decreases when the toner is used for color toners.

In the crosslinking reaction and/or elongation reaction of a polyester prepolymer (A) with an amine (B) to prepare a modified polyester (i), a reaction inhibitor can be used if desired to control the molecular weight of the resultant modified polyester. Specific examples of such a reaction inhibitor include monoamines (e.g., diethyle amine, dibutyl amine, butyl amine and lauryl amine), and blocked amines (i.e., ketimine compounds) prepared by blocking the monoamines mentioned above.

# 10 Unmodified polyester

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The toner for use in the image forming apparatus of the present invention includes not only the modified polyester resins (i) mentioned above, but also an unmodified polyester (ii) serving as a binder resin of the toner. By using a combination of a modified polyester (i) with an unmodified polyester (ii), the low temperature fixability of the toner can be improved and in addition the toner can produce color images having high gloss.

Suitable unmodified polyesters (ii) include

20 polycondensation products of a polyol (PO) with a

polycarboxylic acid (PC). Specific examples of the polyol (PO)

and the polycarboxylic acid (PC) are mentioned above for use
in the modified polyester (i). In addition, specific examples
of the suitable polyol (PO) and polycarboxylic acid (PC) are

25 also mentioned above.

In addition, as the unmodified polyester (ii), polyester resins modified by a bonding (such as urethane bonding) other

than a urea bonding, can also be used as well as the unmodified polyester resins which are not modified at all.

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When a mixture of a modified polyester (i) with an unmodified polyester (ii) is used as the binder resin, it is preferable that the modified polyester (i) at least partially mixes with the unmodified polyester (ii) to improve the low temperature fixability and hot offset resistance of the resultant toner. Namely, it is preferable that the modified polyester (i) has a structure similar to that of the unmodified polyester (ii). The mixing ratio (i/ii) of a modified polyester (i) to an unmodified polyester (ii) is from 5/95 to 80/20, preferably from 5/95 to 30/70, more preferably from 5/95 to 25/75, and even more preferably from 7/93 to 20/80. When the addition amount of the modified polyester (i) is too small, the hot offset resistance of the resultant toner deteriorates and in addition it is hard to impart a good combination of high temperature preservability and low temperature fixability to the resultant toner.

The peak molecular weight of the unmodified polyester

(ii) for use in the toner of the present invention is from 1,000 to 10,000, preferably from 2,000 to 8,000, and more preferably from 2,000 to 5,000. When the peak molecular weight is too low, the high temperature preservability of the toner deteriorates. In contrast, when the peak molecular weight is too high, the low temperature fixability of the toner deteriorates.

It is preferable for the unmodified polyester (ii) to have a hydroxyl value not less than 5 mgKOH/g, preferably from 10

to 120 mgKOH/g, and more preferably from 20 to 80 mgKOH/g. When the hydroxyl value is too low, it is hard to impart a good combination of high temperature preservability and low temperature fixability to the resultant toner.

The unmodified polyester (ii) preferably has an acid value of from 1 to 5 mgKOH/g, and more preferably from 2 to 4 mgKOH/g. In particular, when a wax having a high acid value is used for the toner as a release agent, the binder resin preferably has a low acid value to impart good charging ability and a high resistivity to the resultant toner.

In the toner of the present invention, the binder resin (i.e., the modified polyester and the unmodified polyester) preferably has a glass transition temperature (Tg) of from 35 to 70  $^{\circ}$ C, and preferably from 55 to 65  $^{\circ}$ C. When the glass transition temperature is too low, the high temperature preservability of the toner deteriorates. In contrast, when the glass transition temperature is too high, the low temperature fixability of the toner deteriorates. since a modified polyester resin is used as the binder resin, the resultant toner has better high temperature preservability than conventional toners including a polyester resin as a binder resin even if the modified polyester resin has a relatively low glass transition temperature.

#### Colorant

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The toner of the present invention includes a colorant.

Suitable colorants for use in the toner of the present invention include known dyes and pigments. Specific examples

of the colorants include carbon black, Nigrosine dyes, black iron oxide, Naphthol Yellow S, Hansa Yellow (10G, 5G and G), Cadmium Yellow, yellow iron oxide, loess, chrome yellow, Titan Yellow, polyazo yellow, Oil Yellow, Hansa Yellow (GR, A, RN and R), Pigment Yellow L, Benzidine Yellow (G and GR), Permanent Yellow (NCG), Vulcan Fast Yellow (5G and R), Tartrazine Lake, Quinoline Yellow Lake, Anthrazane Yellow BGL, isoindolinone yellow, red iron oxide, red lead, orange lead, cadmium red, cadmium mercury red, antimony orange, Permanent Red 4R, Para Red, Fire Red, p-chloro-o-nitroaniline red, Lithol Fast Scarlet G, Brilliant Fast Scarlet, Brilliant Carmine BS, Permanent Red (F2R, F4R, FRL, FRLL and F4RH), Fast Scarlet VD, Vulcan Fast Rubine B, Brilliant Scarlet G, Lithol Rubine GX, Permanent Red F5R, Brilliant Carmine 6B, Pigment Scarlet 3B, Bordeaux 5B, Toluidine Maroon, Permanent Bordeaux F2K, Helio Bordeaux BL, Bordeaux 10B, BON Maroon Light, BON Maroon Medium, Eosin Lake, Rhodamine Lake B, Rhodamine Lake Y, Alizarine Lake, Thioindigo Red B, Thioindigo Maroon, Oil Red, Quinacridone Red, Pyrazolone Red, polyazo red, Chrome Vermilion, Benzidine Orange, perynone orange, Oil Orange, cobalt blue, cerulean blue, Alkali Blue Lake, Peacock Blue Lake, Victoria Blue Lake, metal-free Phthalocyanine Blue, Phthalocyanine Blue, Fast Sky Blue, Indanthrene Blue (RS and BC), Indigo, ultramarine, Prussian blue, Anthraquinone Blue, Fast Violet B, Methyl Violet Lake, cobalt violet, manganese violet, dioxane violet, Anthraquinone Violet, Chrome Green, zinc green, chromium oxide, viridian, emerald green, Pigment Green B, Naphthol Green B, Green Gold,

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Acid Green Lake, Malachite Green Lake, Phthalocyanine Green, Anthraquinone Green, titanium oxide, zinc oxide, lithopone and the like. These materials are used alone or in combination.

The content of the colorant in the toner is preferably from 1 to 15 % by weight, and more preferably from 3 to 10 % by weight, based on total weight of the toner.

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Master batch pigments, which are prepared by combining a colorant with a resin, can be used as the colorant of the toner for use in the image forming apparatus of the present invention. Specific examples of the resin for use in the master batch pigments or for use in combination with master batch pigments include the modified and unmodified polyester resins mentioned above; styrene polymers and substituted styrene polymers such as polystyrene, poly-p-chlorostyrene and polyvinyltoluene; styrene copolymers such as styrene-p-chlorostyrene copolymers, styrene-propylene copolymers, styrene-vinyltoluene copolymers, styrene-vinylnaphthalene copolymers, styrenemethyl acrylate copolymers, styrene-ethyl acrylate copolymers, styrene-butyl acrylate copolymers, styrene-octyl acrylate copolymers, styrene-methyl methacrylate copolymers, styrene-ethyl methacrylate copolymers, styrene-butyl methacrylate copolymers, styrene-methyl  $\alpha$ -chloromethacrylate copolymers, styrene-acrylonitrile copolymers, styrene-vinyl methyl ketone copolymers, styrene-butadiene copolymers, styrene-isoprene copolymers, styrene-acrylonitrile-indene copolymers, styrene-maleic acid copolymers and styrene-maleic acid ester copolymers; and other resins such as polymethyl

methacrylate, polybutyl methacrylate, polyvinyl chloride, polyvinyl acetate, polyethylene, polypropylene, epoxy resins, epoxy polyol resins, polyurethane resins, polyamide resins, polyvinyl butyral resins, acrylic resins, rosin, modified rosins, terpene resins, aliphatic or alicyclic hydrocarbon resins, aromatic petroleum resins, chlorinated paraffin, paraffin waxes, etc. These resins are used alone or in combination.

The master batch for use in the toner for use in the image forming apparatus of the present invention is typically prepared by mixing and kneading a resin and a colorant upon application of high shear stress thereto. In this case, an organic solvent can be used to heighten the interaction of the colorant with the resin. In addition, flushing methods in which an aqueous paste including a colorant is mixed with a resin solution of an organic solvent to transfer the colorant to the resin solution and then the aqueous liquid and organic solvent are separated and removed can be preferably used because the resultant wet cake of the colorant can be used as it is. Of course, a dry powder which is prepared by drying the wet cake can also be used as a colorant. In this case, three roll mill can be preferably used for kneading the mixture upon application of high shear stress.

#### Charge controlling agent

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25 The toner for use in the image forming apparatus of the present invention includes a charge controlling agent.

Specific examples of the charge controlling agent include

known charge controlling agents such as Nigrosine dyes, triphenylmethane dyes, metal complex dyes including chromium, chelate compounds of molybdic acid, Rhodamine dyes, alkoxyamines, quaternary ammonium salts (including fluorine-modified quaternary ammonium salts), alkylamides, phosphor and compounds including phosphor, tungsten and compounds including tungsten, fluorine-containing activators, metal salts of salicylic acid, salicylic acid derivatives, etc.

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Specific examples of the marketed products of the charge controlling agents include BONTRON® 03 (Nigrosine dyes), BONTRON® P-51 (quaternary ammonium salt), BONTRON® S-34 (metal-containing azo dye), E-82 (metal complex of oxynaphthoic acid), E-84 (metal complex of salicylic acid), and E-89 (phenolic condensation product), which are manufactured by Orient Chemical Industries Co., Ltd.; TP-302 and TP-415 (molybdenum complex of quaternary ammonium salt), which are manufactured by Hodogaya Chemical Co., Ltd.; COPY CHARGE® PSY VP2038 (quaternary ammonium salt), COPY BLUE® (triphenyl methane derivative), COPY CHARGE® NEG VP2036 and NX VP434 (quaternary ammonium salt), which are manufactured by Hoechst AG; LRA-901, and LR-147 (boron complex), which are manufactured by Japan Carlit Co., Ltd.; copper phthalocyanine, perylene, quinacridone, azo pigments and polymers having a functional group such as a sulfonate group, a carboxyl group, a quaternary ammonium group, etc.

The content of the charge controlling agent is determined depending on the species of the binder resin used, whether or

not an additive is added and toner manufacturing method (such as dispersion method) used, and is not particularly limited. However, the content of the charge controlling agent is typically from 0.1 to 10 parts by weight, and preferably from 0.2 to 5 parts by weight, per 100 parts by weight of the binder resin included in the toner. When the content is too high, the toner has too large charge quantity, and thereby the electrostatic force of a developing roller attracting the toner increases, resulting in deterioration of the fluidity of the toner and decrease of the image density of toner images.

## Release agent

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The toner for use in the image forming apparatus of the present invention includes a release agent. Suitable release agents include waxes having a melting point of from 50 to 120  $^{\circ}$ C. When such a wax is included in the toner, the wax is dispersed in the binder resin and serves as a release agent at a location between a fixing roller and the toner particles. Thereby hot offset resistance can be improved without applying an oil to the fixing roller used.

In the present invention, the melting point of the release agents is measured by a differential scanning calorimeter (DSC). The maximum absorption peak is defined as the melting point.

Specific examples of the release agent include natural waxes such as vegetable waxes, e.g., carnauba wax, cotton wax, Japan wax and rice wax; animal waxes, e.g., bees wax and lanolin; mineral waxes, e.g., ozokelite and ceresine; and petroleum waxes, e.g., paraffin waxes, microcrystalline waxes and

petrolatum. In addition, synthesized waxes can also be used. Specific examples of the synthesized waxes include synthesized hydrocarbon waxes such as Fischer-Tropsch waxes and polyethylene waxes; and synthesized waxes such as ester waxes, ketone waxes and ether waxes. Further, fatty acid amides such as 1,2-hydroxylstearic acid amide, stearic acid amide and phthalic anhydride imide; and low molecular weight crystalline polymers such as acrylic homopolymer and copolymers having a long alkyl group in their side chain, e.g., poly-n-stearyl methacrylate, poly-n-laurylmethacrylate and n-stearyl acrylate-ethyl methacrylate copolymers, can also be used.

The charge controlling agent, and the release agent can be kneaded with a masterbatch and a binder resin. In addition, the charge controlling agent, and the release agent can be added to an organic solvent when the toner constituent liquid is prepared.

## External additive

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The thus prepared toner particles (i.e., the mother toner) may be mixed with an external additive to assist in improving the fluidity, developing property and charging ability of the toner particles. Suitable external additives include particulate inorganic materials. It is preferable for the particulate inorganic materials to have a primary particle diameter of from 5 nm to 2  $\mu$ m, and more preferably from 5 nm to 500 nm. In addition, it is preferable that the specific surface area of such particulate inorganic materials measured by a BET method is from 20 to 500 m<sup>2</sup>/g. The content of the

external additive is preferably from 0.01 to 5 % by weight, and more preferably from 0.01 to 2.0 % by weight, based on total weight of the toner composition.

Specific examples of such inorganic particulate materials include silica, alumina, titanium oxide, barium titanate, magnesium titanate, calcium titanate, strontium titanate, zinc oxide, tin oxide, quartz sand, clay, mica, sand-lime, diatom earth, chromium oxide, cerium oxide, red iron oxide, antimony trioxide, magnesium oxide, zirconium oxide, barium sulfate, barium carbonate, calcium carbonate, silicon carbide, silicon nitride, etc.

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Among these particulate inorganic materials, a combination of a hydrophobic silica and a hydrophobic titanium oxide is preferably used. In particular, when a hydrophobic silica and a hydrophobic titanium oxide each having an average particle diameter not greater than 50 nm are used as an external additive, the electrostatic force and van der Waals' force between the external additive and the toner particles are improved, and thereby the resultant toner has a proper charge quantity. In addition, even when the toner is agitated in a developing device, the external additive is hardly released from the toner particles, and thereby image defects such as white spots and image omissions are hardly produced. Further, the quantity of particles of the toner remaining on image bearing members can be reduced.

When particulate titanium oxides are used as an external additive, the resultant toner can stably produce toner images

having a proper image density even when environmental conditions are changed. However, the charge rising properties of the resultant toner composition tend to deteriorate particularly when the addition amount of the particulate titanium oxide is greater than that of the particulate silica. However, when the content of the hydrophobized silica and hydrophobized titanium oxide is from 0.3 to 1.5% by weight based on the weight of the toner particles, the charge rising properties of the toner do not deteriorate. Namely, good images can be produced by the toner even after long repeated use.

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Then the method for manufacturing the toner for use in the present invention will be explained. However, the manufacturing method is not limited thereto.

(1) At first, toner constituents including a colorant, an unmodified polyester resin, a polyester prepolymer having an isocyanate group, and a release agent are dissolved or dispersed in an organic solvent to prepare a toner constituent liquid.

Suitable organic solvents include organic solvents having a boiling point less than 100  $^{\circ}$ C so that the solvent can be easily removed from the resultant toner particle dispersion.

Specific examples of the organic solvents include toluene, xylene, benzene, carbon tetrachloride, methylene chloride, 1,2-dichloroethane, 1,1,2-trichloroethane, chloroform, monochlorobenzene, dichloroethylidene, methyl acetate, ethyl acetate, methyl ethyl ketone, methyl isobutyl ketone, etc. These can be used alone or in combination. In particular, aromatic solvents such as toluene and xylene, and halogenated

hydrocarbons such as 1,2-dichloroethane, chloroform and carbon tetrachloride are preferably used.

The addition quantity of the organic solvent is from 0 to 300 parts by weight, preferably from 0 to 100 parts by weight and more preferably from 25 to 70 parts by weight, per 100 parts by weight of the polyester prepolymer used.

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(2) Then the toner constituent liquid is emulsified in an aqueous medium in the presence of a surfactant and a particulate resin.

10 Suitable aqueous media include water, and mixtures of water with alcohols (such as methanol, isopropanol and ethylene glycol), dimethylformamide, tetrahydrofuran, cellosolves (such as methyl cellosolve) and lower ketones (such as acetone and methyl ethyl ketone).

The mixing ratio (A/T) of the aqueous medium (A) to the toner constituent liquid (T) is from 50/100 to 2000/100 by weight, and preferably from 100/100 to 1000/100 by weight. When the content of the aqueous medium is too low, the toner constituent liquid cannot be well dispersed, and thereby toner 20 particles having a desired particle diameter cannot be produced. In contrast, when the content of the aqueous medium is too high, the manufacturing cost of the toner increases.

When the toner constituent liquid is dispersed in an aqueous medium, a dispersant can be preferably used to prepare a stable dispersion.

Specific examples of the surfactants include anionic surfactants such as alkylbenzene sulfonic acid salts,  $\alpha$ -olefin sulfonic acid salts, and phosphoric acid salts; cationic surfactants such as amine salts (e.g., alkyl amine salts, aminoalcohol fatty acid derivatives, polyamine fatty acid derivatives and imidazoline), and quaternary ammonium salts (e.g., alkyltrimethyl ammonium salts, dialkyldimethyl ammonium salts, alkyldimethyl benzyl ammonium salts, pyridinium salts, alkyldimethyl benzyl ammonium salts, pyridinium salts, alkyl isoquinolinium salts and benzethonium chloride); nonionic surfactants such as fatty acid amide derivatives, polyhydric alcohol derivatives; and ampholytic surfactants such as alanine, dodecyldi(aminoethyl)glycin, di)octylaminoethyle)glycin, and N-alkyl-N,N-dimethylammonium betaine.

By using a surfactant having a fluoroalkyl group, a good dispersion can be prepared even when a small amount of the surfactant is used. Specific examples of the anionic surfactants having a fluoroalkyl group include fluoroalkyl carboxylic acids having from 2 to 10 carbon atoms and their metal salts, disodium perfluorooctanesulfonylglutamate, sodium 3-{omega-fluoroalkyl(C6-C11)oxy}-1-alkyl(C3-C4) sulfonate, sodium 3-{omega-fluoroalkanoyl(C6-C8)-N-ethylamino}-1-propanesulfonate, fluoroalkyl(C11-C20) carboxylic acids and their metal salts, perfluoroalkyl(C11-C20) sulfonate and their metal salts, perfluoroalkyl(C4-C12) sulfonate and their metal salts, perfluoroactanesulfonic acid diethanol amides, N-propyl-N-(2-hydroxyethyl)perfluorooctanesulfone amide, perfluoroalkyl(C6-C10) sulfoneamidepropyltrimethylammonium salts, salts of perfluoroalkyl(C6-C10)-N-ethylsulfonyl glycin,

monoperfluoroalkyl (C6-C16) ethylphosphates, etc.

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Specific examples of the marketed products of such surfactants having a fluoroalkyl group include SURFLON® S-111, S-112 and S-113, which are manufactured by Asahi Glass Co., Ltd.; FRORARD® FC-93, FC-95, FC-98 and FC-129, which are manufactured by Sumitomo 3M Ltd.; UNIDYNE® DS-101 and DS-102, which are manufactured by Daikin Industries, Ltd.; MEGAFACE® F-110, F-120, F-113, F-191, F-812 and F-833 which are manufactured by Dainippon Ink and Chemicals, Inc.; ECTOP® EF-102, 103, 104, 105, 112, 123A, 306A, 501, 201 and 204, which are manufactured by Tohchem Products Co., Ltd.; FUTARGENT® F-100 and F150 manufactured by Neos; etc.

Specific examples of the cationic surfactants having a

fluoroalkyl group include primary, secondary and tertiary
aliphatic amino acids, aliphatic quaternary ammonium salts
(such as perfluoroalkyl(C6C10)sulfoneamidepropyltrimethylammonium salts), benzalkonium
salts, benzetonium chloride, pyridinium salts, imidazolinium
salts, etc., all of which have a fluoroalkyl group Specific
examples of the marketed products thereof include SURFLON®
S-121 (from Asahi Glass Co., Ltd.); FRORARD® FC-135 (from
Sumitomo 3M Ltd.); UNIDYNE® DS-202 (from Daikin Industries,
Ltd.); MEGAFACE® F-150 and F-824 (from Dainippon Ink and
Chemicals, Inc.); ECTOP® EF-132 (from Tohchem Products Co.,
Ltd.); FUTARGENT® F-300 (from Neos); etc.

In addition, particulate polymers can be added to stabilize the resultant mother toner particles formed in an

aqueous medium. Therefore it is preferable that a particulate polymer is added to the aqueous medium such that the surface of the mother toner particles are covered with the particulate polymer at a covering ratio of from 10 to 90 %.

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Specific examples of the particulate polymers include particulate polymethyl methacylate having a particle diameter of from 1 to 3 µm, particulate polystyrene having a particle diameter of from 0.5 to 2 µm, particulate styrene-acrylonitrile copolymers having a particle diameter of 1 µm, etc. Specific examples of the marketed particulate polymers include PB-200H (from Kao Corp.), SGP (Soken Chemical & Engineering Co., Ltd.), TECHNOPOLYMER® SB (Sekisui Plastics Co., Ltd.), SPG-3G (Soken Chemical & Engineering Co., Ltd.), MICROPEARL® (Sekisui Fine Chemical Co., Ltd.), etc.

In addition, an inorganic dispersant can be added to the aqueous medium. Specific examples of the inorganic dispersants include tricalcium phosphate, calcium carbonate, titanium oxide, colloidal silica, hydroxyapatite, etc.

Further, it is possible to stably disperse toner constituents in an aqueous medium using a polymeric protection colloid in combination with the inorganic dispersants and/or particulate polymers mentioned above. Specific examples of such protection colloids include polymers and copolymers prepared using monomers such as acids (e.g., acrylic acid, methacrylic acid,  $\alpha$ -cyanoacrylic acid,  $\alpha$ -cyanomethacrylic acid, itaconic acid, crotonic acid, fumaric acid, maleic acid and maleic anhydride), acrylic monomers having a hydroxyl group

(e.g.,  $\beta$ -hydroxyethyl acrylate,  $\beta$ -hydroxyethyl methacrylate,  $\beta$ -hydroxypropyl acrylate,  $\beta$ -hydroxypropyl methacrylate,  $\gamma$ -hydroxypropyl acrylate,  $\gamma$  -hydroxypropyl methacrylate, 3chloro-2-hydroxypropyl acrylate, 3-chloro-2-hydroxypropyl 5 methacrylate, diethyleneglycolmonoacrylic acid esters, diethyleneglycolmonomethacrylic acid esters, glycerinmonoacrylic acid esters, N-methylolacrylamide and N-methylolmethacrylamide), vinyl alcohol and its ethers (e.g., vinyl methyl ether, vinyl ethyl ether and vinyl propyl ether), 10 esters of vinyl alcohol with a compound having a carboxyl group (i.e., vinyl acetate, vinyl propionate and vinyl butyrate); acrylic amides (e.g, acrylamide, methacrylamide and diacetoneacrylamide) and their methylol compounds, acid chlorides (e.g., acrylic acid chloride and methacrylic acid 15 chloride), and monomers having a nitrogen atom or an alicyclic ring having a nitrogen atom (e.g., vinyl pyridine, vinyl pyrrolidone, vinyl imidazole and ethylene imine).

(e.g., polyoxyethylene, polyoxypropylene,
20 polyoxyethylenealkyl amines, polyoxypropylenealkyl amines,
 polyoxyethylenealkyl amides, polyoxypropylenealkyl amides,
 polyoxyethylene nonylphenyl ethers, polyoxyethylene
 laurylphenyl ethers, polyoxyethylene stearylphenyl esters,
 and polyoxyethylene nonylphenyl esters); and cellulose
25 compounds such as methyl cellulose, hydroxyethyl cellulose and
 hydroxypropyl cellulose, can also be used as the polymeric

protective colloid.

In addition, polymers such as polyoxyethylene compounds

The dispersion method is not particularly limited, and low speed shearing methods, high speed shearing methods, friction methods, high pressure jet methods, ultrasonic methods, etc. can be used. Among these methods, high speed shearing methods are preferable because particles having a particle diameter of from 2  $\mu$ m to 20  $\mu$ m can be easily prepared. At this point, the particle diameter (2 to 20  $\mu$ m) means a particle diameter of particles including a liquid).

When a high speed shearing type dispersion machine is used, the rotation speed is not particularly limited, but the rotation speed is typically from 1,000 to 30,000 rpm, and preferably from 5,000 to 20,000 rpm. The dispersion time is not also particularly limited, but is typically from 0.1 to 5 minutes. The temperature in the dispersion process is typically from 0 to 150 °C (under pressure), and preferably from 40 to 98 °C.

(3) At the same time when a toner constituent is dispersed in an aqueous medium, an amine (B) is added to the aqueous medium to be reacted with the polyester prepolymer (A) having an isocyanate group.

This reaction accompanies crosslinking and/or elongation of the molecular chains of the polyester prepolymer (A). The reaction time is determined depending on the reactivity of the amine (B) with the polyester prepolymer used, but is typically from 10 minutes to 40 hours, and preferably from 2 to 24 hours. The reaction temperature is from 0 to 150 °C, and preferably from 40 to 98 °C. In addition, known catalysts such as dibutyltin laurate and dioctyltin laurate, can be used for the

reaction, if desired.

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(4) After the reaction, the organic solvent is removed from the resultant dispersion (emulsion, or reaction product), and then the solid components are washed and then dried. Thus, a mother toner is prepared.

In order to remove the organic solvent, all the system is gradually heated while agitated so as to form laminar flow. Then the system is strongly agitated in a certain temperature range, followed by solvent removal, to prepare a mother toner having a spindle form.

In this case, when compounds such as calcium phosphate which are soluble in an acid or alkali are used as a dispersion stabilizer, it is preferable to dissolve the compounds by adding an acid such as hydrochloric acid, followed by washing of the resultant particles with water to remove calcium phosphate therefrom. In addition, calcium phosphate can be removed using a zymolytic method.

(5) Then a charge controlling agent is fixedly adhered to the mother toner. In addition, an external additive such as combinations of a particulate silica and a particulate titanium oxide is adhered to the mother toner to prepare the toner of the present invention.

Addition of the charge controlling agent and the external additive to the mother toner can be made using a known method using a mixer or the like.

By using this manufacturing method, the resultant toner can have a relatively small particle diameter and a narrow

particle diameter distribution. By controlling the strong agitation during the solvent removing process, the shape of the toner can be controlled so as to be a desired form of from a rugby ball form to a true spherical form. In addition, the surface condition of the toner can also be controlled so as to be a desired surface of from a smooth surface and a roughened surface.

The toner for use in the image forming apparatus of the present invention has substantially a spherical form satisfying the following relationships:

- $0.5 \le r2/r1 \le 1.0$ ; and
- $0.7 \le r3/r2 \le 1.0$ ,

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wherein r1 represents a major-axis particle diameter of the toner, r2 represents a minor-axis particle diameter of the toner and r3 represents a thickness of the toner, wherein r3  $\leq$  r2  $\leq$  r1.

Figs. 7A to 7C are schematic views illustrating a typical toner particle of the toner for use in the present invention. As illustrated in Figs. 7A to 7C, when the major-axis particle diameter of the toner is represented by r1, the minor-axis particle diameter of the toner is represented by r2 and the thickness of the toner is represented by r3, the ratio (r2/r1) is preferably from 0.5 to 1.0 and the ratio (r3/r2) is preferably from 0.7 to 1.0.

When the ratio (r2/r1) is too small (i.e., the particle form of the toner is apart from the true spherical form), the dot reproducibility and the transferability of the toner

deteriorate, and thereby high quality image cannot be produced. In addition, when the ratio (r3/r2) is to small, the transferability of the toner deteriorates because the toner has a flat form. In particular, it is preferable that the ratio (r3/r2) is 1.0, because the toner can be rotated around the major axis thereof. In this case, the toner has good fluidity.

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The particle diameters r1, r2 and r3 of a toner are determined by observing 100 toner particles with a scanning electron microscope while the viewing angle is changed.

The thus prepared toner can be used as a magnetic or non-magnetic one-component developer including no magnetic carrier.

When the toner is used for a two-component developer, the toner is mixed with a magnetic carrier. Suitable magnetic carriers include ferrite and magnetite including a divalent metal atom such as Fe, Mn, Zn and Cu. The volume average particle diameter of the carrier is preferably from 20 to 100 µm. When the particle diameter is too small, a problem in that the carrier tends to adhere to the photoreceptor during the developing process occurs. In contrast, when the particle diameter is too large, the carrier is not mixed well with the toner, and thereby the toner is insufficiently charged, resulting in formation of undesired images such as images with background development.

Among the carrier materials mentioned above, Cu-ferrite including Zn is preferable because of having a high saturation magnetization. However, the carrier is not limited thereto,

and a proper carrier is selected depending on the developing device of the image forming apparatus of the present invention.

The surface of the carrier can be coated with a resin such as silicone resins, styrene-acrylic resins, fluorine-containing resins and olefin resins. Such a resin is coated on a carrier typically by the following method:

- (1) a coating resin is dissolved in a solvent to prepare a coating liquid; and
- (2) the coating liquid is coated on carrier particles, for example, by a spraying method using a fluidized bed.

Alternatively, the resin can also be coated by the following method:

- (1) a resin is electrostatically adhered to the surface of carrier particles; and
- 15 (2) the resin is heated to be fixed on the surface of the carrier particles.

The thickness of the thus formed resin layer on the carrier particles is from 0.05 to 10  $\mu\text{m}\textsc{,}$  and preferably from 0.3 to 4  $\mu\text{m}\textsc{.}$ 

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## Effects of the present invention

As can be understood from the above-description, the cleaner of the charging device of the present invention for cleaning a charging roller can efficiently remove foreign materials (such as reversely-charged toner particles and paper dust) adhered to the surface of the charging roller over a long period of time. Therefore, the charging roller can maintain

good charging ability over a long period of time. When the charging device having a cleaner of the present invention is used for an image forming apparatus, good images can be produced without causing charging problems such as uneven charging.

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This document claims priority and contains subject matter related to Japanese Patent Application No. 2003-055090, filed on March 3, 2003, incorporated herein by reference.

Having now fully described the invention, it will be
apparent to one of ordinary skill in the art that many changes
and modifications can be made thereto without departing from
the spirit and scope of the invention as set forth therein.